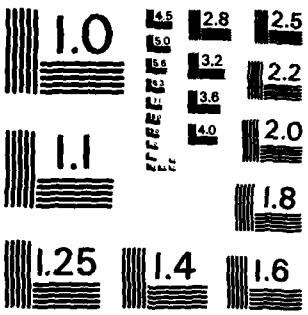
AD-A130 629 OPTICAL WAVEGUIDE GAS SENSORS(U) NAVAL RESEARCH LAB 1/1
WASHINGTON DC J F GIULIANI ET AL. 13 JUL 83 NRL-TR-1

UNCLASSIFIED F/G 9/1 NL

END
DATE FILMED
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS - 1963 - A

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

(2)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report #1, 6170:616:NJ:yl	2. GOVT ACCESSION NO. AD-A130629	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Optical Waveguide Gas Sensors		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report 1 Nov. 82 - 31 May 83
		6. PERFORMING ORG. REPORT NUMBER Technical Report #1
7. AUTHOR(s) J.F. Giuliani, H. Wohltjen and N.L. Jarvis		8. CONTRACT OR GRANT NUMBER(s) USAFSAM JON 2739-01-04
9. PERFORMING ORGANIZATION NAME AND ADDRESS Naval Research Laboratory Washington, DC		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS TSQ 83-6
11. CONTROLLING OFFICE NAME AND ADDRESS U.S. Air Force School of Aerospace Medicine Brooks Air Force Base, Texas		12. REPORT DATE 13 July 1983 13. NUMBER OF PAGES 6
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified 15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Prepared for publication in the American Chemical Society Monograph MICROSENSORS FOR CHEMICAL ANALYSIS.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Optical waveguide
coatings
surface

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The discoveries of solid organic film coatings exhibiting color change reactions to specific vapors have made it possible to detect weak surface chemical reactions at the film-vapor interface by means of a multiple reflecting optical probe. A brief review of total multiple reflection and the application of two prototype devices built at NRL for the detection of low concentrations of ammonia and organophosphonate vapors is presented. Preliminary data characterizing both devices with regards to vapor response, reversibility, etc., will be discussed. Several design modifications are suggested to improve our devices.

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

S/N 0102-LF-014-6601

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

AD A130629

DTIC FILE COPY

DTIC ELECTE JUL 22 1983 S D E

83 07 22 040

U.S. AIR FORCE SCHOOL OF AEROSPACE MEDICINE

Project No. TSQ 83-6

TECHNICAL REPORT NO. 1

Optical Waveguide Gas Sensors

by

J.F. Giuliani
H. Wohltjen
N.L. Jarvis

Prepared for Publication in the American Chemical Society Monograph: Microsensors for Chemical Analysis.

Naval Research Laboratory
Washington, DC 20375

12 July 1983

Accession For
NTIS GRA&I [X]
DTIC TAB [ ]
Unannounced [ ]
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A

Approved for public release; distribution unlimited.

Optical Waveguide Gas Sensors

J.F. Giuliani, H. Wohltjen and N.L. Jarvis

Naval Research Laboratory
Washington, DC 20375

ABSTRACT

The development of small, portable and rugged devices for detecting low concentrations of toxic vapors has rapidly accelerated within the last several years due to advances in microfabrication and miniaturization techniques in optics and electronics. Moreover, the discoveries of solid organic film coatings exhibiting color change reactions to specific vapors, have made it possible to detect weak surface chemical reactions at the film-vapor interface by means of a multiple reflecting optical probe. A brief review of total multiple reflection and the application of two prototype devices built at NRL for the detection of low concentrations of ammonia and organophosphonate vapors is presented. Preliminary data characterizing both devices with regards to vapor response, reversibility, etc., will be discussed. Several design modifications are suggested to improve our devices.

INTRODUCTION

It is well known from geometrical optics that when a light beam is internally reflected from the surface of an optically transparent dense medium, such as glass, at angles exceeding the critical angle, total reflection at the glass-air interface occurs. From a wave optics point of view, a superposition of the incoming waves with the reflected waves forms a standing wave pattern perpendicular to the glass-air interface. At this

interface there is both a sinusoidal variation of the electric field amplitude with distance from the reflecting glass medium, and a slowly decaying electric field whose amplitude exponentially decreases with distance from the glass surface into the air. This non-propagating wave is termed the ''evanescent wave'', and it is used as a sensitive probe of the glass-air interface. If a thin solid or liquid film is applied to the glass surface then the evanescent wave can, in principle, probe the film-air interface. If a vapor is introduced into the air above the film, and if the film is known to react with the vapor to produce a modification of the film's absorption coefficient or refractive index, then this surface reaction will be sensed by the evanescent wave.

The degree of interaction between the evanescent wave and the film-vapor interface can be determined from Fresnel's equations (1). The solutions to these equations, however, give little physical insight and it is more informative to look at the evanescent wave probe interaction from a more phenomenological point of view. Hence, for the case of a weakly absorbing film in contact with a glass rod, the reflection coefficient at the film-air interface can be written as

$$R = 1 - \alpha\, de. \tag{1}$$

Here, α is the absorption coefficient of the film, and de is termed the effective thickness, and is equal to the thickness required to yield the same absorption loss in a transmission measurement. This effective thickness is thus a measure of the strength of the interaction of the evanescent wave with the film. There are two extreme film thickness conditions which can modify the effective thickness de: 1) for films much thicker than several microns, de is limited by the evanescent penetration depth dp and is given by

$$de = \frac{\eta_{21}\, Eo^2 dp}{2 \cos \theta} . \tag{2}$$

Here η_{21} is the refractive index ratio at the air-film interface, Eo is the light field amplitude at the film interface for an incident wave having unit amplitude, dp is the penetration depth of the evanescent wave into the film, and is the angle of incidence. 2) For films much thinner than the penetration depth of the evanescent wave, the effective thickness is

$$de = \frac{\eta_{21}\, Eo^2 d_f}{\cos \theta} . \tag{3}$$

Here, d_f is the actual film thickness. Experimental data relating detector response to ammonia vapor as a function of film thickness will be displayed later in this paper.

Finally, it can be shown that the effective thickness de and hence the strength of the interaction between the evanescent probe beam and the vapor-sensitive film may be enhanced through multiple reflections at the film-air interface. Thus, the reflection power for N reflections can be incorporated into ''equation 1'' and is given for a weakly absorptive film by

$$R^N = (1-\alpha de)^N \simeq 1-\alpha N de. \qquad (4)$$

''Equation 4'' brings out the most important feature of an optical device based on multiple total reflection, and that is the ability to amplify many orders of magnitude, very small changes produced in de or α which may occur between an organic solid film and a vapor in a surface reaction.

OPTICAL WAVEGUIDE GAS SENSORS

The first report of a practical organic-film-coated optical waveguide sensor for toxic vapor detection was published by Hardy et al (2) in 1975. A picrate dye was employed as the selective chemical indicator for cyanide vapors. Subsequently, David et al (3) and Orofino et al (4) described similar devices incorporating a ninhydrin-coated quartz solid rod that could detect ammonia vapor concentrations down in the parts per billion range.

OPTICAL WAVEGUIDE AMMONIA GAS SENSOR

In 1983 we at NRL reported an ammonia vapor device (5) based on the latest techniques of solid state electronics and miniaturized optical components. Our device was a practical improvement over the foregoing devices in that the organic chemical sensitive coating showed reversibility to ammonia vapors over many vapor/air cycles, and use was made of a capillary tube configuration, which allows for more than 600 optical reflections to be achieved over a 9 cm length. Moreover, the electronic packaging required only a few square centimeters of space, and was battery powered. The simplicity and ruggedness of this device makes it useful for portable point detection in environmental monitoring applications. Details of the device, and preliminary device response and sensitivity data were presented in (5). For this paper, additional data is presented which illustrates the important roles of water vapor, and film thickness for the detection of ammonia vapors.

Figures 1 and 2 illustrate both the combined effects of water vapor and film thickness on the detection level limits of anhydrous ammonia vapors. For the case shown in figure 1, the thickness of the dye film coating was estimated to be less than one micron. As is evident, a relative humidity of 40 percent limits the lowest detection level for anhydrous ammonia vapors to about 60 ppm. However, for the case of a dye film thicker than a few microns, as shown in figure 2, the sensitivity limit to anhydrous ammonia vapors in dry air, i.e., 2 to 3 percent water vapor, reaches levels in the parts per million range, as would be predicted from ''equation 2''. In this case, the evanescent probe wave samples a larger thickness of the dye film. However, the increased sensitivity to ammonia can be more than offset by a 40 percent relative humidity, which as shown in figure 2, completely masks the ammonia response over the same concentration range shown in figure 1.

Preliminary kinetic data of the relative response of our device to high concentrations of ammonia vapors, or saturated air (i.e., 80 percent water vapor) is shown in figure 3, for a thick dye film coating. Note particularly the slower rise time of the water vapor response as compared to the ammonia vapor response. These curves suggest a possible discrimination time scheme for the separation of the two interfering effects.

ORGANOPHOSPHONATE OPTICAL WAVEGUIDE VAPOR SENSOR

Recently, we have coated a capillary tube surface with an organic dye which is known to produce a color change when reacted with organophosphonate compounds. This dye is an ethyl analogue of Michler's Ketone, (i.e., 4,4-bis diethylamino benzophenone) also called ''EMKO'' (6).

Figure 4 shows the optical density as a function of wavelength before (A) and after (B) reaction with 1 mg of an organophosphonate simulant, methane sulfonyl chloride (CH_3SO_2Cl), with a 9% solution of ''EMKO'' in acetone.

Note the significant growth in the absorption edge in the bluer spectral region and a small red band around 600 nm. These spectral changes result in the observed pale yellow color after reaction (B). This ''EMKO'' solution was evaporated onto a capillary and incorporated into the optical waveguide system described in (5). Figure 5 displays the response of our device to the simulant vapors under dry air conditions. The data points are a composite of many different film coatings and simulant-dry air cyclings. Concentrations down to below 10 ppm are achieved. Although the dye coating is selective to this toxic vapor, there are a number of practical limitations, including ''shelf-life'', photo-chemical degradation, reversibility and to a lesser extent,

its thermal stability. With respect to the photo-chemical degradation problem, we have repeated and extended the investigations reported by Poziomek et al (7) to excitation wavelengths at 560 nm and 650 nm. Changes in the optical spectra for ''EMKO'' as a function of the excitation wavelength are shown in figure 6. Here, the change in optical density over the visible spectral region is plotted for a 10 percent EMKO/MeOH solution, irradiated at 325 nm, 560 nm and 650 nm, respectively, for three hours at each excitation wavelength. As can be seen, irradiation at 325 nm produces a significant increase in the UV absorption edge, in addition to a weak band around 425 nm, confirming the results of Poziomek et al (7). On the other hand, exciting a previously non-irradiated sample at 650 nm for three hours, while not affecting the UV portion of the visible spectrum, does however, produce a new weak IR band around 650 nm. This is interesting, since the organophosphonate simulant (i.e. CH_3SO_2Cl) also produces an IR band around 650 nm when reacted with this dye. Lastly, excitation of this dye with 560 nm light for three hours, appears to produce no significant absorption changes in the visible spectrum from that of the non-irradiated solution shown in figure 6. Consequently, the 560 nm LED source used in our optial waveguide device to probe the simulant vapor-dye film reaction produced no photo-degradation of the film coating.

The shelf-life of this oxime dye solution was determined to be about three months when kept out of direct sunlight and stored in a dry, cool air environment. It should be noted at this point, that the detection of the simulant vapor by our device was done under dry conditions (i.e., at 6% to 8% relative humidity), and at room temperature. Some preliminary data has been obtained at humidity levels between 47 percent and 56 percent. Our results show that at these moist air conditions, the response of this dye is reduced by three to four times that of the dry air response. Also, the dye film becomes completely unreactive after only two dry air-wet air cycles. This effect is attributed to a hydrolysis reaction between the dye and water vapor, which in turn produces an irreversible colorless reaction product.

CONCLUSIONS AND COMMENTS

The data presented here clearly indicate the practical application of multiple-reflecting optical waveguide devices as sensitive vapor sensors. The data also show that detection below parts per million has not yet been achieved. However, most of the limitations of our devices are not fundamental in nature and can be solved through improved engineering design which include low noise and low drift light sources, differential detection, and better shielded low drift amplifiers and electrical connections. Moreover, a significant increase in optical amplification and hence a greater sensitivity to weak vapor-film

surface reactions can be easily achieved using longer waveguide pathlengths. Finally, it should be possible to produce a vast array of inexpensive, selective, and compact optical waveguide gas sensors, from the largely untapped thousands of organic compounds which exhibit absorption changes or shifts in the presence of toxic vapors.

ACKNOWLEDGEMENT

The authors wish to express their thanks to the U.S. Air Force, School of Aerospace Medicine, Brooks Air Force Base, for their support of this work.

REFERENCES

1. Harrick, N.J., ''Internal Reflection Spectroscopy'', Interscience Publishers, Div. J. Wiley and Sons, NY, 1967.

2. Hardy, E.E., David, D.J., Kapany, N.S., and Unterleitner, F.C., Nature, 1975, 257, 666.

3. David, D.J., Willson, M.C., and Ruffin, D.S., Anal. Lett. 1976, 389.

4. Orofino, T.A., David D.J. and Hardy, E.E., ''A Technique for Work-Station Monitoring Utilizing Optical Waveguides'', 4th Joint Conference on Sensing Environmental Pollutants, New Orleans, LA, 1977, 374.

5. Giuliani, J.F., Wohltjen, H. and Jarvis, N.L., Optics Letters 1983, 8, 54.

6. Kramer, D.N., Morin, R.D., and Poirier, R.H., U.S. Patent No. 2,926,072, (1959); U.S. Patent No. 2,929,791, (1959).

7. Poziomek, E.J., Fentiman, A.F. and Poirier, R.H., Microchemical Journal 1970, 15, 475.

Figure 1. Optical transmittance change at 560 nm versus anhydrous ammonia vapor concentration plotted at a vapor flow rate of 0.3 liter/min. at ambient dry air at 27°C. The dotted line represents the transmittance change response of the device to water vapor at 40% RH only. The film coating thickness is less than one micron.

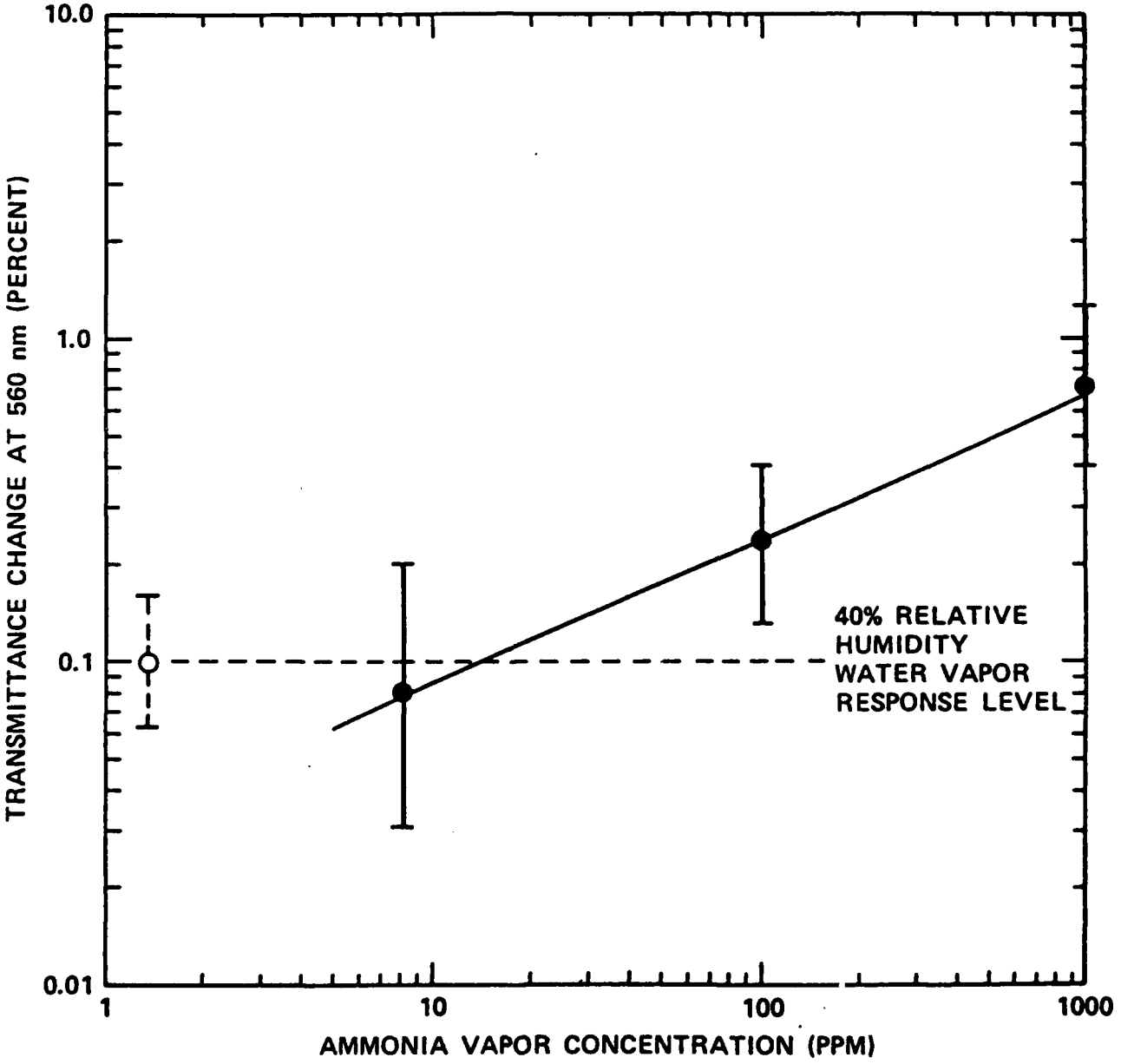
Figure 2. Optical transmittance change at 560 nm versus anhydrous ammonia vapor concentration under the same experimental conditions as in figure 1, but for a dye film thickness of a few microns. Note, that the transmittance change at 40% RH for water vapor, produces a detector response which completely obscures the ammonia vapor signal below 1000 ppm.

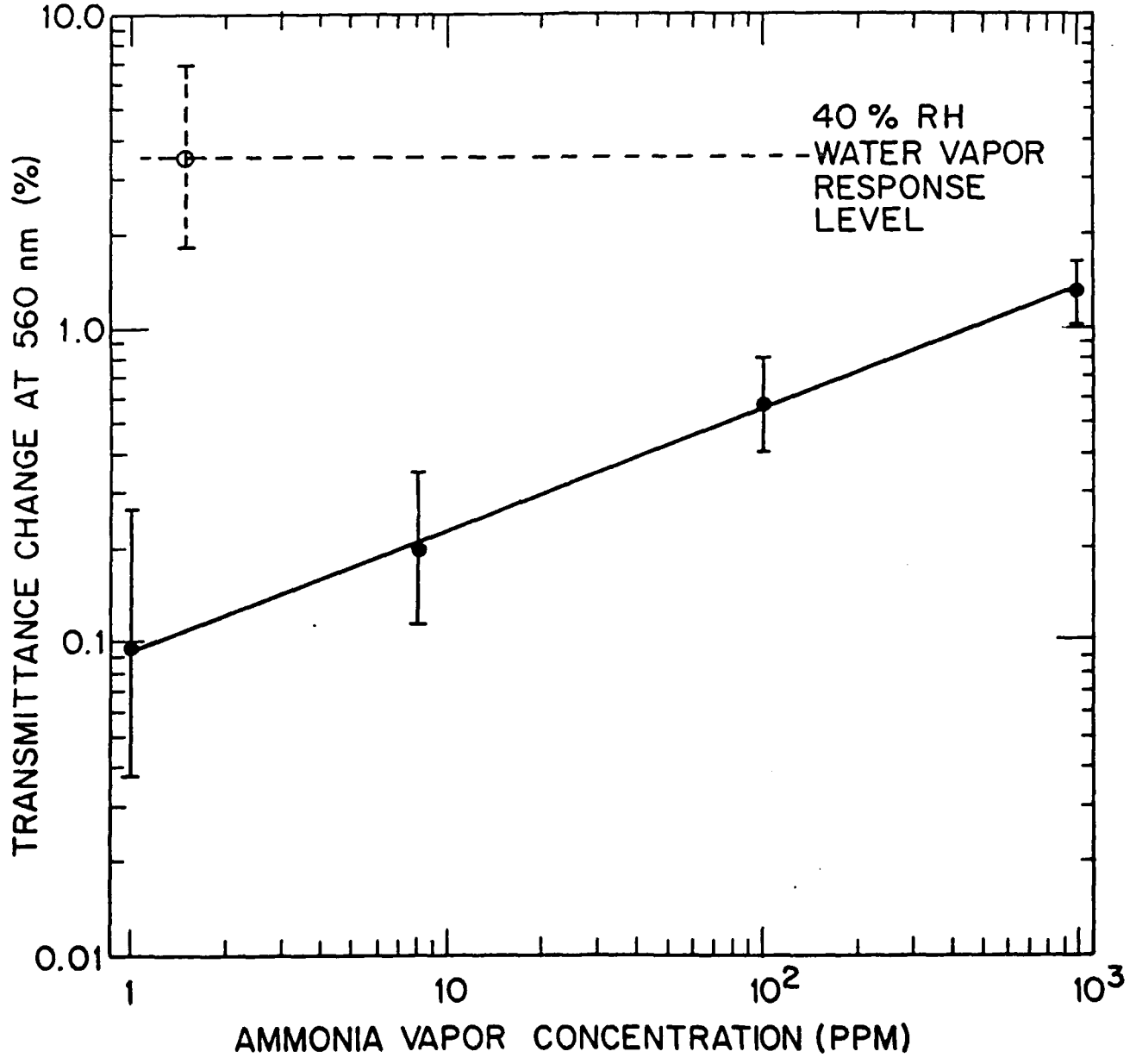
Figure 3. Kinetic response of the thick film-coated, optical waveguide device to a high concentration of ammonia vapor or water vapor. Note the faster response of the device to ammonia as compared with water vapor.

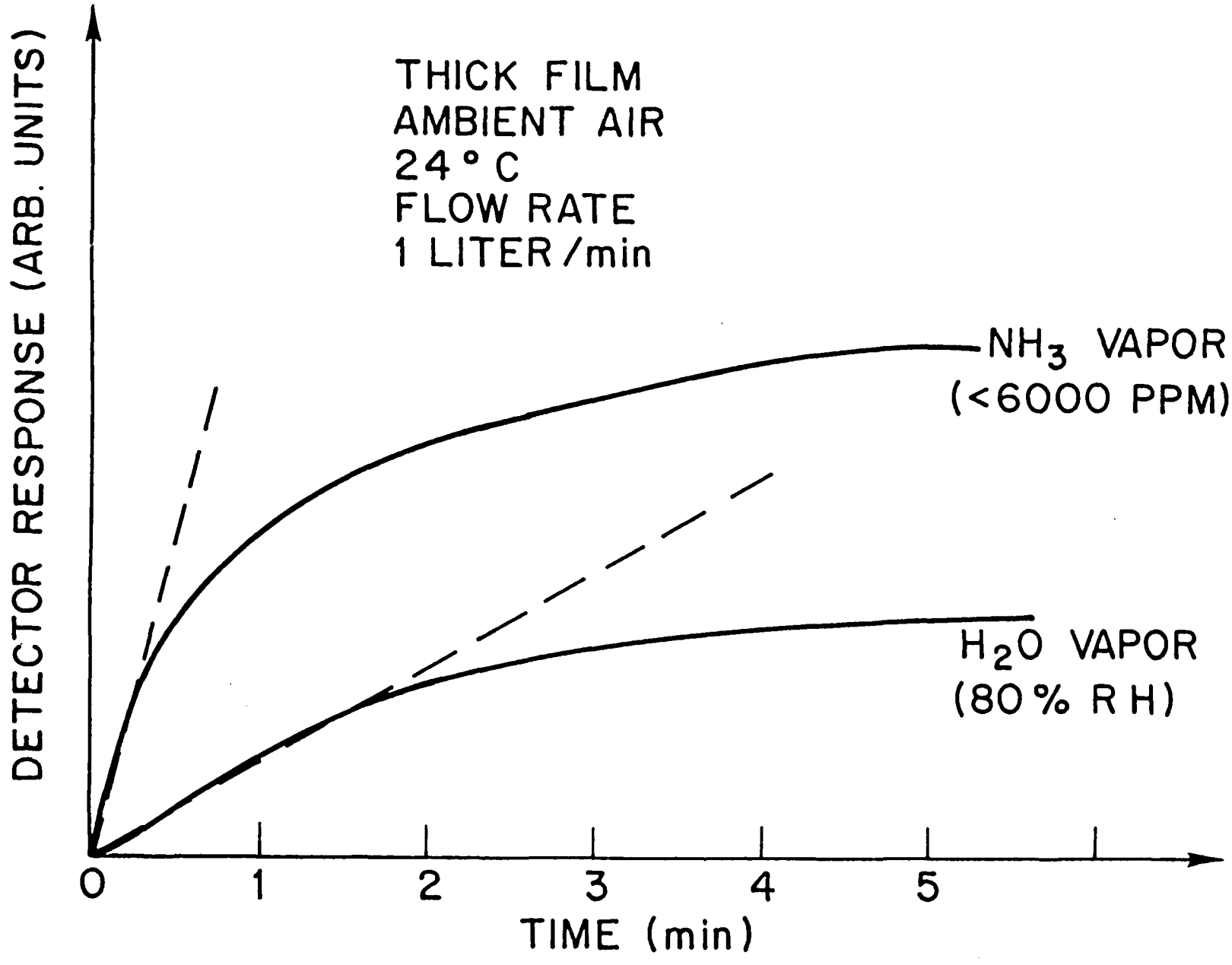
Figure 4. Optical density changes over the visible spectrum for a solution of EMKO in acetone, before and after the injection of an organophosphonate simulant into the solution.

Figure 5. Optical waveguide detector response to the organophosphonate simulant.

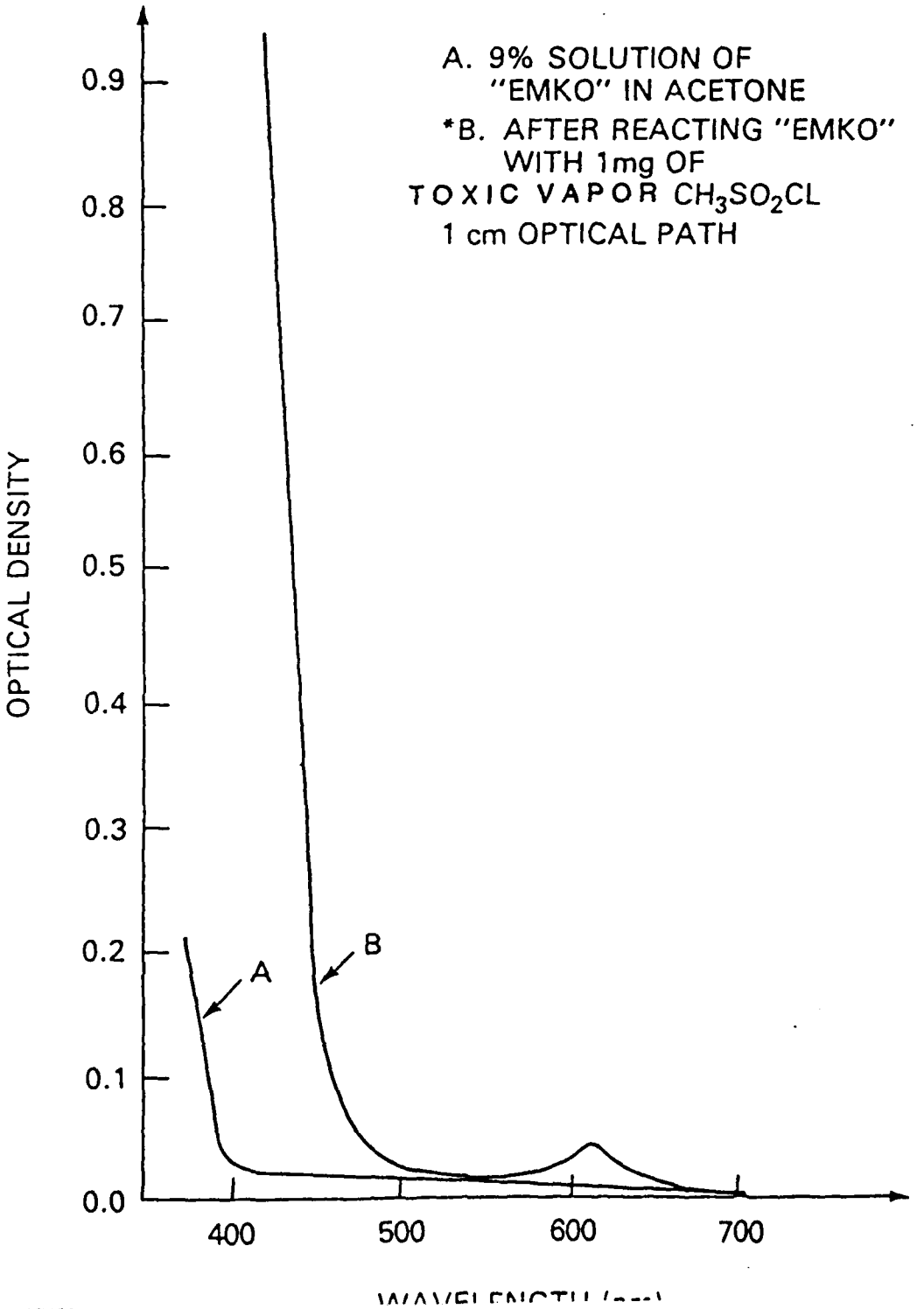
Figure 6. Photochemical changes in the optical density over the visible spectrum as a function of three excitation wavelengths.

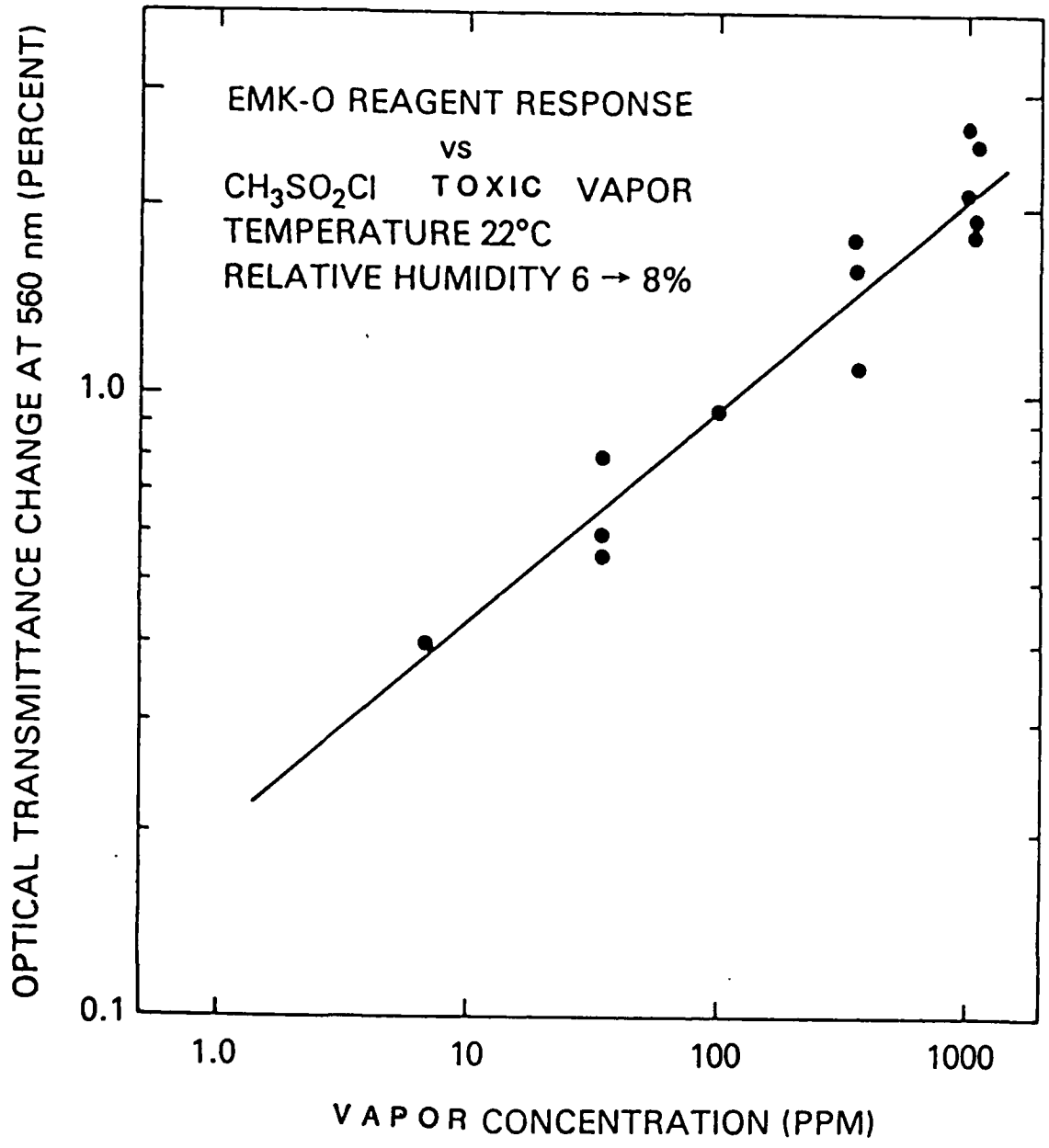

10.0
1.0
0.1
0.01
TRANSMITTANCE CHANGE AT 560 nm (PERCENT)
1
10
100
1000
AMMONIA VAPOR CONCENTRATION (PPM)
40% RELATIVE HUMIDITY WATER VAPOR RESPONSE LEVEL

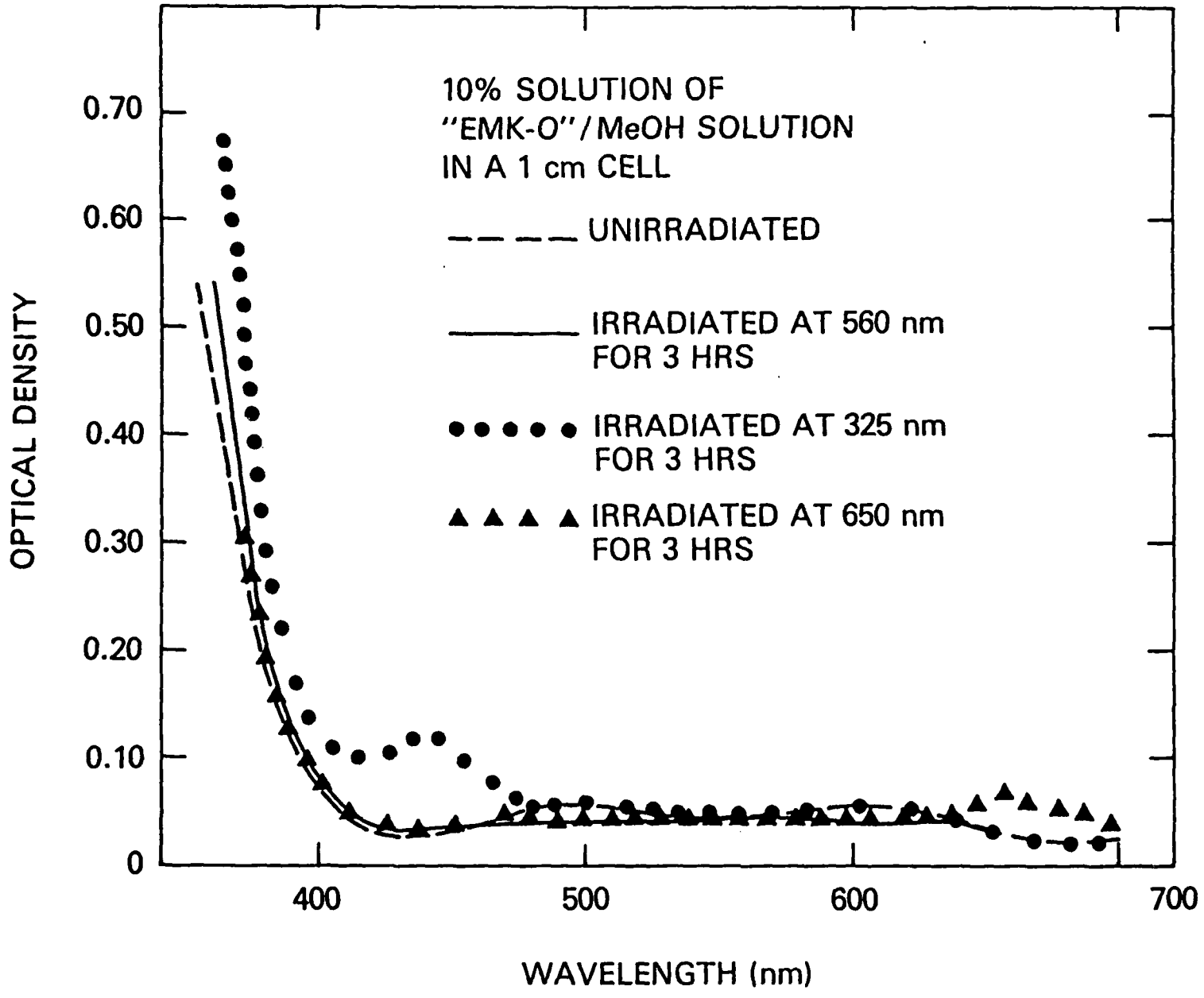

10.0
1.0
0.1
0.01
TRANSMITTANCE CHANGE AT 560 nm (%)
40 % RH
WATER VAPOR
RESPONSE
LEVEL
1
10
10^2
10^3
AMMONIA VAPOR CONCENTRATION (PPM)


DETECTOR RESPONSE (ARB. UNITS)
THICK FILM
AMBIENT AIR
24° C
FLOW RATE
1 LITER/min
NH3 VAPOR
(<6000 PPM)
H2O VAPOR
(80% RH)
0
1
2
3
4
5
TIME (min)

ORGANOPHOSPHORUS VAPOR DETECTING DYE




EMK-O REAGENT RESPONSE
vs
CH_3SO_2Cl TOXIC VAPOR
TEMPERATURE 22°C
RELATIVE HUMIDITY 6 → 8%
OPTICAL TRANSMITTANCE CHANGE AT 560 nm (PERCENT)
1.0
0.1
1.0
10
100
1000
VAPOR CONCENTRATION (PPM)


10% SOLUTION OF
"EMK-O"/MeOH SOLUTION
IN A 1 cm CELL
UNIRRADIATED
IRRADIATED AT 560 nm
FOR 3 HRS
IRRADIATED AT 325 nm
FOR 3 HRS
IRRADIATED AT 650 nm
FOR 3 HRS
OPTICAL DENSITY
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0
400
500
600
700
WAVELENGTH (nm)

END

DATE
FILMED

8 — 83

DTIC